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Review

A review of oxyhalide disinfection by-products determination in water by ion chromatography and ion chromatography-mass spectrometry

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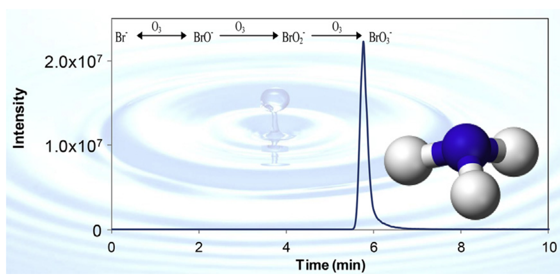
HIGHLIGHTS

- A critical review of IC-MS and its application to inorganic oxyhalide disinfection by-products.
- Comparison of reported method performances at the μg/L level.
- Future directions for fast, multi-analyte analysis by IC-MS.

GRAPHICAL ABSTRACT



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ABSTRACT

This paper is a review of ion chromatographic (IC) separations of inorganic oxyhalide disinfection by-products (DBPs) in water and beverages. The review outlines the chemical mechanisms of formation, regulation of maximum allowable levels, chromatographic column selection and speciation. In addition, this review highlights the application of IC coupled to mass spectrometry (MS) for trace and elemental composition analysis of oxyhalides, along with the analytical considerations associated to enable sensitive analysis. Furthermore, a review of literature concerning IC determination of inorganic oxyhalide DBPs in environmental matrices, including water, published since 2005 is presented, with a focus on MS detection, and a discussion on the relative performance of the methods. Finally some prospective areas for future research, including fast, selective, multi-analyte analysis, for this application are highlighted and discussed.

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1. Introduction

Disinfection by-product (DBP) risk management is a major challenge for water suppliers. Disinfectants can react with naturally-occurring materials in water to form chemical by-products, which pose potential adverse health risks.

The primary requirements for water treatment are to remove organic matter, inorganic species and micropollutants as well as to preserve the purified water for human consumption. The two main options for water disinfection are chlorination and ozonation. Whilst chlorination is the more historic and widely utilised of the two, ozonation offers several advantages, such as destruction of a wider range of organisms and the removal of tastes and odours. Even using ozonation, chlorine is still required during the process for water preservation. However, elevated drinking water occurrence of chlorate (ClO_3^-; *m/z* 83), chlorite (ClO_2^-; *m/z* 67), perchlorate (ClO_4^-; *m/z* 99) and also bromate (BrO_3^-; *m/z* 128) have been identified as chlorine dioxide or ozonation DBPs formed during water treatment, generally at the μg–mg/L level [1,2]. This has resulted in significant research efforts to understand their environmental occurrence, fate and risk to humans especially *via* drinking water sources. In addition to this, it is also essential to monitor the quality of bottled beverages, such as fruit juices, to ensure the ingredient water, as well as the finished product, complies with the regulations and is safe for human consumption. The presence and levels of these DBPs will depend on the disinfection process used, as well as the chemicals already present within the source water. Several, more detailed reviews on the disinfection of water, and formation of DBPs and their potential health impacts on humans are available elsewhere and so only warrant a summary discussion here [3,4].

Alongside other techniques, the analytes of interest, bromate, chlorate and perchlorate, have been routinely and widely determined by ion chromatography (IC) for over 20 years, and a review in 2005 by Michalski discussed the analysis of inorganic oxyhalide DBPs using IC with conductivity, UV/Vis and mass spectrometry (MS) detection [4]. The ability to speciate gives IC an obvious advantage over several other analytical techniques, such as various spectroscopic methods including atomic spectroscopy. Speciation can be vital when it comes to the identification and characterisation of oxyhalides, such as in the differentiation of oxychloride species (i.e. ClO_3^-, ClO_4^-) from the free chloride ion.

The aims of this review are to (a) detail the existing (IC(-MS)) methods available from a perspective of inorganic DBPs analysis since 2005; and (b) discuss potential directions for IC-MS technologies to further advance methods in terms of analysis time, sensitivity, specificity and target analytes, for the analysis of oxyhalide DBPs.

2. Formation and regulation of bromate, chlorate and perchlorate in water

2.1. Bromate

Bromate is formed when water containing bromide is exposed to disinfection using the ozonation process. This process infuses ozone into the water in order to remove the organic and inorganic pollutants present *via* oxidation and filtration/sedimentation.

A mechanism by which bromate is formed was proposed by Legube et al. and is shown in Fig. 1 [5]. The researchers state that reactions between ozone, bromide and hypobromite are relatively slow at low temperatures, but they are also dependent on the pH of the water and concentration of bromide (typically between trace-0.5 mg/L concentrations in fresh water [6]). Bromate can also be formed when disinfecting drinking water using concentrated sodium hypochlorite. Bromide is present in both the chlorine and sodium hydroxide used to form hypochlorite, and is quickly converted to bromate at the high pH of the solution (a 10–15% solution of hypochlorite has a pH ~13) [7]. Once formed, bromate is very stable in water, and difficult to remove.

The International Agency for Research on Cancer (IRAC) has classified bromate in group 2B as a possible carcinogen to humans. Using the available information, the European Commission and the US Environmental Protection Agency (EPA) have set a maximum allowable level (MAL) of 10 μg/L in drinking water. The U.S. Food and Drug Administration (FDA) adopted the EPA levels for bromate and chlorite in 2001 as some food and beverage companies use ozonation or other disinfection treatments on their products [8]. This was also the case for residual disinfectants, chlorine, chlorine dioxide and chloramines. Despite these regulatory levels, in a 2005 study by Snyder et al., the concentration of bromate exceeded this limit in three of the 21 tested bottled waters in the US with the highest concentration found to be 76 μg/L, almost eight times the MAL [9].

2.2. Chlorate

Chlorate, and also chlorite, are DBPs either formed by the decomposition of sodium hypochlorite, shown in the reaction below, or alternatively when chlorine, chlorine dioxide or chloramine is used to disinfect drinking water.

$$2ClO^- \rightarrow Cl^- + ClO_2^- \quad (1)$$

$$ClO^- + ClO_2^- \rightarrow Cl^- + ClO_3^- \quad (2)$$

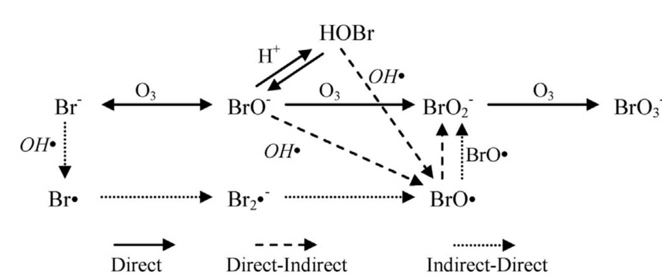

Fig. 1. Bromate formation pathways during ozonation. Adapted from [5]